



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> HARD MATERIAL COATING WITH YTTRIUM AND METHOD FOR ITS DEPOSITION  <b>(57) Abstract</b>  Ternary hard material layers are described to which a small proportion of yttrium is added to increase the resistance to wear at elevated temperatures.		

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## HARD MATERIAL COATING WITH YTTRIUM AND METHOD FOR ITS DEPOSITION

The invention relates to PVD hard coating materials for engineering components used in a hot environment, especially for tools for the coolant-free and lubricant-free machining of materials.

The coolant-free and lubricant-free machining of materials, in particular of metals like die steels or aluminium alloys, is increasingly gaining in significance, in particular in the automotive industry.

TiN and TiCN layers deposited by the known PVD and CVD methods cannot satisfy this object satisfactorily because both begin to oxidize at operating temperatures beyond 400°C and thus considerable wear arises, in particular at the cutting edges. This is because the oxides which are formed are very brittle and spall off from the TiN or TiCN coating due to their low bond strength and different thermal expansion. This leads to a continuous and considerable reduction of the layer thickness in the edge region during cutting operations at elevated temperatures. Analogous effects can also arise with forming tools.

It has been found that TiAlN applied by the PVD process as a hard material coating is much better suited to resisting the oxidation processes. It has been reported that the temperature at which oxidation sets in can be increased to 700 to 800°C when the hard material layer consists, for example, of

50 at % Ti and of 50 at % Al. (W.-D. Münz, J. Vac. Sci. Technol., A4 (6) (1986) 2117).

Even higher Al contents have been reported, i.e. Al contents of up to 70 at % of the respective metal content. It is known from the field of turbine blade coating that the addition of yttrium increases the oxidation resistance of superalloys such as CoCrAlY or of thermally insulating layers of zirconium oxide.

In the hard material coating field a layer of TiYN has admittedly been reported with a Y-content of more than 10 at %; however, this layer proved to be unsuitable for industrial use, mainly because of its brittleness. (J.R. Roos, J.P.Celis, E. Vancoille, H. Veltrop, S. Boelens, F. Jungblut, J. Ebberink, H. Homberg, Thin Solid Films, 193/194 (1990) 1542).

An object of the invention is to thermally stabilize the interface between the hard material coating and the respective substrate and to further reduce the onset of oxidation.

For this purpose the invention proposes the addition of small quantities of yttrium to binary, ternary or quaternary TiAl-based multi-component layers. Preferably the yttrium is unevenly distributed with respect to the growth direction of the coating. That means that the distribution is not uniform perpendicular to the substrate surface.

In particular, pure yttrium or alloys containing yttrium and scandium, are added to today's well known TiAlN.

In accordance with the invention yttrium is preferably added in the concentration range between 0.1 to 4.0 at % in ternary TiAlN alloys or in TiAlN/CrN, TiAlN/ZrN, TiAlN/TiN, TiAlN/MoN

and TiAlN/WN multi-layer coatings. It will be understood that the percentage value of yttrium is quoted as a percentage of the metallic constituents only. Preferably a Y-content of only 1.5 to 2.0 at % of the Ti and Al constituents is recommended and used.

The coating of the tools is preferably produced by sputtering (unbalanced magnetron UBM) (W.-D. Münz, Surf. Coat. Technol., 48(1991) 81), cathodic arc evaporation (e.g. steered arc) or with combination methods as cathodic arc evaporation/sputtering (W.-D. Münz, D. Schulze, F.J.M. Hauzer, Surf. Coat. Technol., 50 (1992) 169) or sputtering/low voltage electron beam evaporation (anodic arc evaporation) or combined low voltage evaporation/cathodic arc evaporation.

The uneven or non-uniform distribution of yttrium in the growth direction of the hard coating is achieved by the special choice of the deposition conditions. It has to be stated that the lateral distribution of the yttrium parallel to the substrate surface has to be as uniform as possible. The uneven distribution in growth direction is obtained by using a multitarget unbalanced magnetron sputtering machine. Fig. 1 shows the cross-section of an industrial four target PVD coater (detailed description: W.-D. Münz, D. Schulze, F.J.M. Hauzer, Surf. Coat. Technol., 50 (1992) 169). Four cathodes are mounted vertically into the doors of the vacuum chamber. The cathodes are of linear design. Four rectangular targets with a typical dimension of 60 cm x 20 cm (target thickness: 1-2 cm) are mounted on the four cathodes. The substrates to be coated are mounted on a rotating turntable as shown in Fig. 1. They are subjected to a three-fold planetary rotation as outlined by the arrows in Fig. 1. During coating they are passing all four cathodes collecting vaporised atoms sputtered from the cathodes. If a uniform distribution of an alloy material is required all four targets should be mounted

with identical sputtering materials. In case of the TiAlN deposition all four cathodes should be equipped with targets of the same composition.

It is a preferred feature of the invention to avoid yttrium being incorporated over the entire hard material layer thickness with high uniformity as would be the case if the yttrium would be distributed in equal concentrations over all targets in a multi-target deposition system involved in the deposition process.

Thus, according to the invention the yttrium is unevenly distributed over the entire hard material layer thickness and this special distribution can be obtained in a multi-target deposition system in which the yttrium is not alloyed into all targets and preferably only into a single target.

Advantageous embodiments of the invention are described in the subclaims and will be explained in the following description of examples in connection with Figures 1 to 8.

When using multi-target deposition systems with the yttrium being distributed in equal concentrations over all targets involved in the deposition process of TiAlN, it can be shown that yttrium is incorporated over the entire hard material layer with high uniformity.

Whereas this may influence the formation of dense oxide layers on top of the hard nitride coating positively, e.g. on TiAlN, it must be stated that there is destabilisation of the interface between the nitride coating and the substrate taking place with increasing temperatures. It was only possible to prevent this destabilisation by the described uneven distribution of the Y in the growth direction of the coating.

In detail the following target assembly has been used. To carry out the combined steered arc/unbalanced magnetron deposition process, one cathode was equipped with a Cr target. The Cr target was used to perform the metal-ion-etch process in a steered arc discharge to establish in vacuo a clean substrate surface. Cr was chosen as target material to reduce the generation of droplets which deposit on the substrate surface and cause growth defects there in the deposited TiAlN (W.-D. Münz, I.v. Smith, L.A. Donohue, V.S. Brooks, German Patent Application 195 47 305.1) or TiAlYN coating. Two targets consisted of 50 at % Ti and 50 at % Al. The Y-containing target with typically 48 at % Ti, 48 at % Al and 4 at % Y was mounted between the two TiAl targets.

Fig. 1 describes the actual target assembly. A schematic process sequence is outlined in Fig. 2. It can be seen there also that the deposition of the hard coating with the unbalanced magnetron starts initially without using the TiAlY target. It has been found that the deposition of a pure TiAlN base layer enhances the adhesion of a TiAlN based quaternary coating like TiAlNbN or as in the case described here with TiAlYN. It has also to be mentioned that the Cr cathode was used during the deposition of TiAlN and TiAlYN in the unbalanced magnetron mode on a very low power level. Whereas the TiAl and TiAlY targets were operated with 8 to 10 kW, the Cr target was powered with 0.2 to 1 kW, typically with 0.5 kW. Initially, it was thought to prevent cross-contamination from the TiAl targets. However, it has been found out surprisingly that a low chromium content of the coating led to an increase of the oxidation resistance when compared to a pure TiAlN coating. A detailed set of coating parameters is given in Table 1.

Process Steps	Units	Parameter Range	Recommended Conditions
<u>Substrate Heat-up</u> Temperature	°C	250 - 550	450
<u>Metal Ion Etch</u> Target Material	at %	100 Cr or 100 Mo	100 Cr
Pressure Argon	mbar	0 - $5 \cdot 10^{-3}$	$0.3 - 0.6 \times 10^{-3}$
Current	A	50 - 200	100
Substrate Bias	V	-1800 to -1500	-1200
Temperature	°C	350 - 550	420 - 450
Duration	min	1-20	10
<u>Deposition Base</u> Layer (UBM)			
Pressure total (Ar + N <sub>2</sub> )	mbar	$2-10 \times 10^{-3}$	$3.15 \times 10^{-3}$
Pressure Ar	mbar	$1.5 - 9 \times 10^{-3}$	$3.25 \times 10^{-3}$
Number UBM cathodes		2	2
Power per TiAl cathode	kW	6 - 12	8
Power Cr Cathode	kW	0 - 1.5	0.5
Bias Voltage	V	-50 to -100	-75
Bias Current Density	mA/cm <sup>2</sup>	2 - 5	3
Temperature	°C	350 - 550	420 - 450
Thickness	µm	0.1 - 2	0.2
<u>Deposition of TiAlYN</u> Pressure total (Ar+N <sub>2</sub> )	mbar	$2-10 \times 10^{-3}$	$3.5 \times 10^{-3}$
Pressure Ar	mbar	$1.5 - 9 \times 10^{-3}$	$3.25 \times 10^{-3}$
Power TiAl (2x)	kW	6 - 12	8
Power TiAlY (1x)	kW	6 - 12	8
Power Cr	kW	0.2 - 1.5	0.5
Bias Voltage	V	-50 to -100	-75
Bias Current Density	mA/cm <sup>2</sup>	2 - 5	3
Temperature	°C	350 - 550	420 - 450
Thickness	µm	2 - 6	3 - 5
<u>Cooling down of</u> <u>Substrate</u> Temperature	°C	150 - 300	200+

Table 1: Important Process Parameters for a Four Cathode Combined Arc/Unbalanced Magnetron PVD Coating Machine with a Typical Target Size of 60 cm x 20 cm



When using the "preferred deposition conditions" as outlined in Table 1 the following film composition of the metallic constituents of the hard material coating has been found by using WDX (Wavelength Dispersive X-Ray Analysis):

40 at % Ti

56 at % Al

2 at % Y

2 at % Cr

The stabilisation of the interface between the hard coating and a steel substrate by the uneven incorporation of Y is shown in Figs. 3 to 5 using SNMS (Secondary Neutral Mass Spectroscopy) analyses.

Fig. 3 shows the completely uniform distribution of the coating constituents Al(4), Ti(6), Cr(7), N(3) over the complete thickness range. The intensity of the metal concentration is given in non-calibrated counts. In this coating no Y was incorporated. Therefore Y is only identified as a low concentrated random element. The sample has been heat treated for one hour in air at 800°C. Despite this heat treatment a sharp decay of the Fe signal (8) is observed at the interface indicating that no significant diffusion of Fe into the hard coating has taken place. Only a rather thin oxide layer is formed on top of the TiAlN coating as indicated by the sharp increase of the oxygen signal (1) and the parallel decrease of the N signal (3). However, if one increases the heat treatment temperature to 900°C a significant diffusion of Fe (6) into the coating is observed (Fig. 4). The formation of a surface oxide layer is intensified. Concluding from the shape of signal 4 (Al), 5 (Ti), 1(O) and 3 (N) an almost N-free oxide is formed with an Al rich top layer and a Ti rich oxide between the Al-oxide and the TiAlN film. The formation of this N-free sandwich oxide on top of a TiAlN coating has been

confirmed by earlier work (D. McIntyre, J.E. Greene, G. Håkansson, J.-E. Sundgren, W.-D. Münz, J. Appl. Phys. 67 (1990) 1542). Extrapolation from the observed data (point "A" in Fig. 4) allow the estimation of an oxide thickness of 0.8  $\mu\text{m}$ . The uneven incorporation of Y into the coating completely changes the results gained by SNMS analyses (Fig. 5). Similar to the case at 800°C a steep decay of the Fe signal /6 is observed at the interface thus demonstrating clearly that the Fe diffusion is completely suppressed. The Y itself seem to be distributed uniformly between the top oxide and the interface. SNMS does not permit the resolution of the layered and therefore uneven incorporation of Y into the coating. Because of the rotation of the substrate holders the Y concentration may be regarded as a layered concentration, e.g. varying approximately sinusoidally in the growth direction. SNMS shows only that the Al rich oxide is more or less Y-free and that there exists some indication that Y is incorporated into the Ti oxide portion. It can also be seen that the thickness of the sandwich oxide is reduced by the incorporation of Y to an approximate thickness of 0.65  $\mu\text{m}$ .

The positive influence of low concentrated Y but also of Cr onto the oxidation resistance respectively onto the formation of a passivating oxide coating on top of the hard nitride coating has been established by TG (Thermo Gravimetric) analyses, too. Fig. 6 shows isotherms recorded at a temperature of 900°C and over a reaction time in air up to 10 hours. It can be clearly seen that 2 at % Cr already reduce the weight gain due to oxidation during the reaction of TiAlN with hot air. However, the most pronounced improvement was found when Y was added in the "uneven" mode into the coating. For comparison reasons the oxidation behaviour of TiN is given in Fig. 6 also. One recognises a steep increase in weight gain due to the spontaneous formation of  $\text{TiO}_2$  at 900°C. The coating is completely oxidised already after 1

hour. Therefore no further weight gain is observed due to the fact that the stainless steel substrate material oxidises only marginally in this temperature range.

The discrete concentration of Y into one target led to a substantial influence of the growth mechanism of the coating.

Coatings without Y showed in X-ray analyses with pronounced  $\langle 111 \rangle$  preferred orientation. Fig. 7a exhibits an XRD diagram of a  $\text{Ti}_{0.42}\text{Al}_{0.58}\text{N}$  coating. The XRD diagram of  $\text{TiAlN}$  with continuous Y distribution is very similar although the peaks are somewhat broader, indicating higher internal stresses and smaller grain size of the polycrystalline coating.

Incorporating Y from one single target completely changes the XRD spectrum. The  $\langle 111 \rangle$  preferred orientation is converted into a  $\langle 200 \rangle$  preferred orientation with much less sharp peaks as shown in Fig. 7b. Both the broader peaks and the  $\langle 200 \rangle$  preferred orientation indicate smaller grain sizes and continuous re-nucleation of the growing film.

It has been found that the above described drastic thermal stabilisation of the interface can - for example - be achieved under target arrangement conditions as described in Fig. 1. It is also important to note that linear cathodes allow a very uniform distribution of the Y content parallel to the substrate surface and across the full height of the cathode length as compared to cathode arrangements with a series of small circular cathodes as very often used in cathodic arc evaporation systems.

The assumption of a continuous re-nucleation and grain refinement caused by the uneven distribution of Y in the growth

direction of the coating can be strengthened by cross-section TEM (Transmission Electron Microscopy) analyses.

Figs. 8a and 8b show computer processed TEM images which show in Fig. 8a the typical columnar growth of TiAlN coatings as reported in earlier work (G. Håkansson, J.-E. Sundgren, D. McIntyre, E. Greene, W.-D. Münz, Thin Solid Films, 153 (1987) 55).

Fig. 8b however demonstrates a very fine grained film growth with clear indications of regular columnar growth only in the direct vicinity of the interface. In this section of the coating the base layer was deposited as outlined in Fig. 2. Fig. 8b supports also the understanding of reduced oxidation of Y containing TiAlN coating due to the obviously prolonged diffusion paths for oxygen along the reduced grain sizes. It is also common knowledge that fine grained hard coatings are subjected to high internal stresses. The TEM results therefore justify the introduction of the Y-free base layer since via this graded interface the influence of the internal stresses onto the adhesion of the coatings should be reduced. The higher internal stresses of the fine grained TiAlN may be quantified also by an enhanced hardness HK 2700 in comparison to the Y-free coating with typically HK 2400.

Experiments showed that the achievements generated by the described incorporation of Y can be improved further when Yttrium is alloyed with Scandium. A typical composition of 50 at % Y and 50 at % Sc has been found to have a significant effect.

Furthermore, it has been shown that the hard material layer should itself be very smooth (W.-D. Münz, I.V. Smith, L.A. Donohue, J.S. Brooks, Patent Application 195 47 305.1) in order to bring about the advantageous influence of the yttrium.

With a surface roughness in the range  $R_a = 0.150$  to  $0.3 \mu\text{m}$ , produced for example by droplet formation during cathodic arc discharge evaporation, the improvement of the cutting behaviour of twist drills in uncooled operation is rather limited. With a roughness of  $R_a < 0.050 \mu\text{m}$  one could, however, find substantial improvements of the service life.

The following tests were made for twist drills:

tool	twist drills 8 mm diameter
blind holes	27 mm in diameter
material machined	GG25 (test iron)
cutting speed	60 m/min
feed	0.2 mm/revolution

The drilling tests brought the following results:

drill uncoated	17 holes
drill TiAlN ( $R_a = 0.15 - 0.20 \mu\text{m}$ )	100 holes
drill TiAlN ( $R_a \leq 0.05 \mu\text{m}$ )	250 holes
drill TiAlYN ( $R_a \leq 0.05 \mu\text{m}$ )	600 - 1,100 holes

References

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German Patent Application 195 47 305.1

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D 44 05 477 A1

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W.-D. Münz

J. Appl. Phys. 67(1990) 1542

G. Håkansson, J.-E. Sundgren, D. McIntyre, J.E. Greene,

W.-D. Münz

Thin Solid Films, 153 (1987) 55

Patent Claims

1. Hard material coatings manufactured by means of cathodic arc evaporation or sputtering or combination processes of sputtering/cathodic arc evaporation or sputtering/low voltage electron beam evaporation or low voltage evaporation/cathodic arc evaporation and consisting substantially of a binary, ternary or quaternary hard material layer comprising nitride or carbonitride, characterised in that the layer contains about 0.1 to 4 at % yttrium.
2. Hard material coating in accordance with claim 1, characterised in that the layer consists substantially of the ternary hard material layer  $\text{TiAlN}$  with an Al-content of 10 to 70 at % and in that 0.1 to 4 at % yttrium is added to this layer.
3. Hard material coating in accordance with claim 2, characterised in that the layer consists of a polycrystalline fcc structure (B1-NaCl-type) with a  $\langle 200 \rangle$  preferred orientation.
4. Hard material coating in accordance with claim 2 or claim 3, characterised in that the intensities of the major XRD peaks from the pattern (111), (220), (311) are smaller than that of the (200) peak intensity by at least 70 %.
5. Hard material coating in accordance with any of the claims 2, 3 or 4, characterised in that the full width at half maximum (FWHM) of the (200) XRD peak is larger than  $1^\circ$  of  $2\theta$ .

6. Hard material coating in accordance with claim 2 or claim 3, characterised in that the yttrium is unevenly distributed in the growth direction of the coating.
7. Hard material coating in accordance with any one of the preceding claims, characterised in that the yttrium content amounts to approximately 1.5 to 2.0 at %.
8. Hard material coating in accordance with any one of the preceding claims, characterised in that the yttrium is replaced by an alloy of yttrium and scandium.
9. Hard material coating in accordance with any one of the preceding claims, characterised in that the scandium content amounts to 50 at %.
10. Hard material coating in accordance with any one of the preceding claims, characterised in that the base layer adjacent the substrate contains substantially no yttrium.
11. Hard material coating in accordance with any one of the preceding claims, characterised in that the coating consists of a multi-layer superlattice of TiAlN/TiN, TiAlN/ZrN, TiAlN/CrN, TiAlN/MoN, TiAlN/WN with an Y content of 0.1 to 4 at %.
12. Hard material coating in accordance with any one of the preceding claims, characterised in that the coating consists of a multi-layer superlattice of TiAlN/TiN, TiAlN/ZrN, TiAlN/CrN, TiAlN/MoN, TiAlN/WN, whereby the Y is incorporated in the TiAlN layers of the superlattice coating.



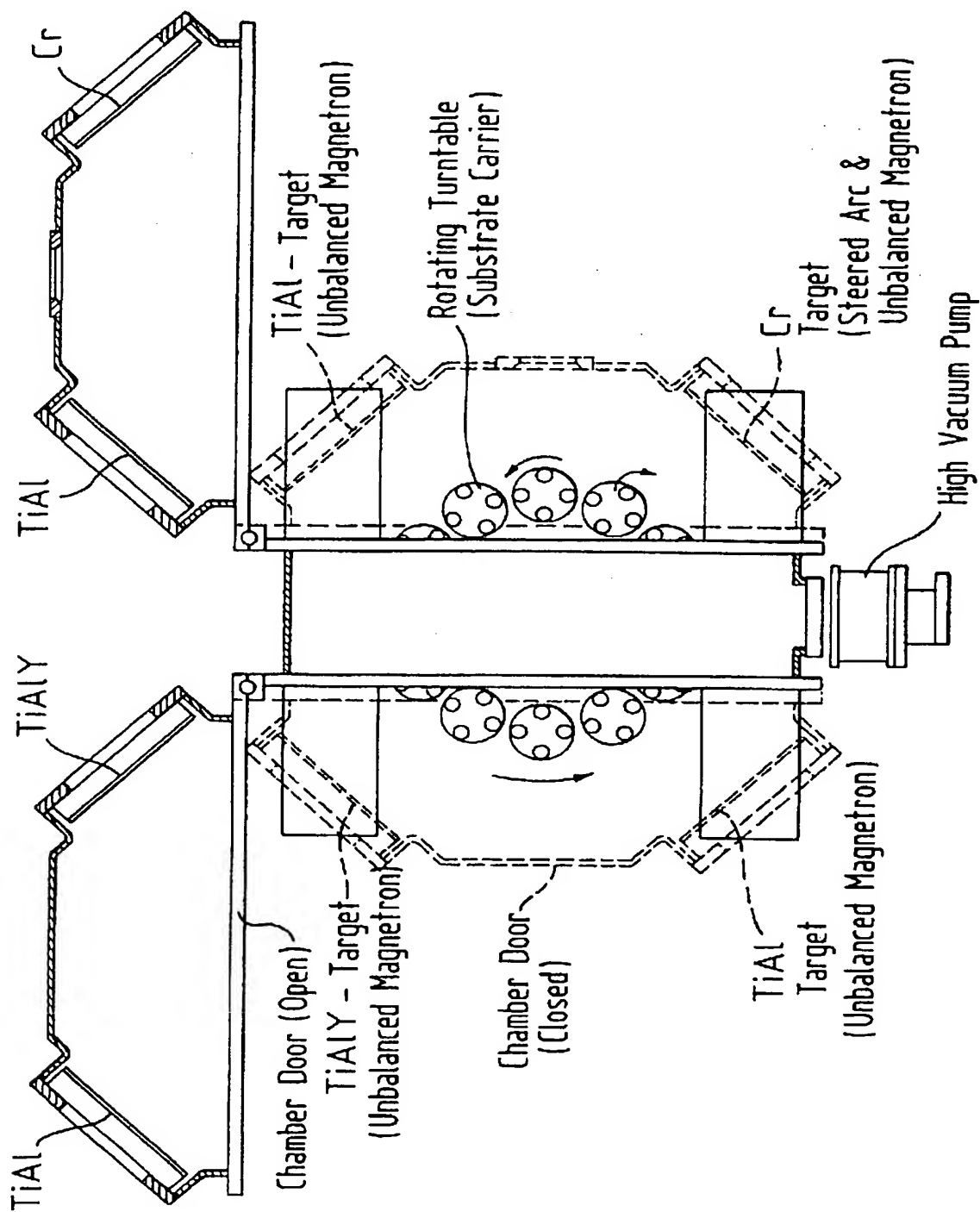
13. Hard material coating in accordance with one of the preceding claims, characterised in that 1 to 10 at %, preferably 2 at % of the total metal content consist of Cr.
14. Hard material coating in accordance with claim 13, characterised in that Cr is used in place of yttrium.
15. Hard material coating in accordance with one of the preceding claims, characterised in that an additional carbon content from 30 to 70 at % is present in the layer.
16. Hard material coating in accordance with claim 15, characterised in that the carbon is exclusively introduced into the outer layer zone and the layer thickness of the outer layer zone amounts to 0.5 to 1  $\mu\text{m}$ .
17. Hard material coating in accordance with one of the preceding claims, characterised in that the total layer thickness of the hard PVD coating amounts to approximately 1.5 to 5  $\mu\text{m}$  independently of the composition of the layer.
18. Hard material coating in accordance with one of the preceding claims, characterised in that the surface roughness of the hard PVD layer on a substrate polished to Ra 0.010  $\mu\text{m}$  amounts preferably to Ra 0.050  $\mu\text{m}$  and smaller values.
19. Hard material coating in accordance with one of the preceding claims, characterised in that the substrate material consists of high-speed steel (HSS) or hard metal (cemented carbide) and the parts to be coated are especially formed by twist drills, milling cutters, reamers,

exchangeable cutting tips or forming tools such as stamping punches or forging dies.

20. PVD-method for coating substrates with a hard material coating in accordance with one of the preceding claims, characterised by the use of multi-target deposition systems in which at least one of the cathodes is not equipped with a Y containing target and the substrates to be coated are mounted on rotatable substrate fixturing systems so that the substrates are intermittently exposed to the Y containing target.
21. Method according to claim 20, wherein the coating is deposited in a four target combined arc/unbalanced magnetron PVD deposition machine having four cathodes, especially four vertically arranged linear cathodes, only one of which is equipped with a Y containing target and the substrates to be coated are mounted on a rotatable substrate fixturing system allowing at least twofold substrate rotations.
22. Method according to claim 20 or 21, characterised in that one of the cathodes being used as a cathodic arc etching cathode, is especially equipped with a Cr target, whereas the other three cathode positions are furnished with TiAl targets and only one of these three cathodes is equipped with a Y containing target.
23. Method in accordance with claim 22, characterised in that Cr is mixed into at least one of the TiAl targets of a multi-target PVD coating machine, in particular an arc coating machine, and is optionally used in place of yttrium.

24. Method in accordance with any one of the claims 19 to 23, characterised in that the cathode behind the target containing yttrium is first switched on after the deposition of a base layer on the substrate containing substantially no yttrium, i.e. only yttrium present as an impurity rather than as an intentional constituent of the layer.

Fig. 1 PVD Coating System  
(Cross Section)



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**Fig. 2**  
Deposition Process  
(Schemetically)

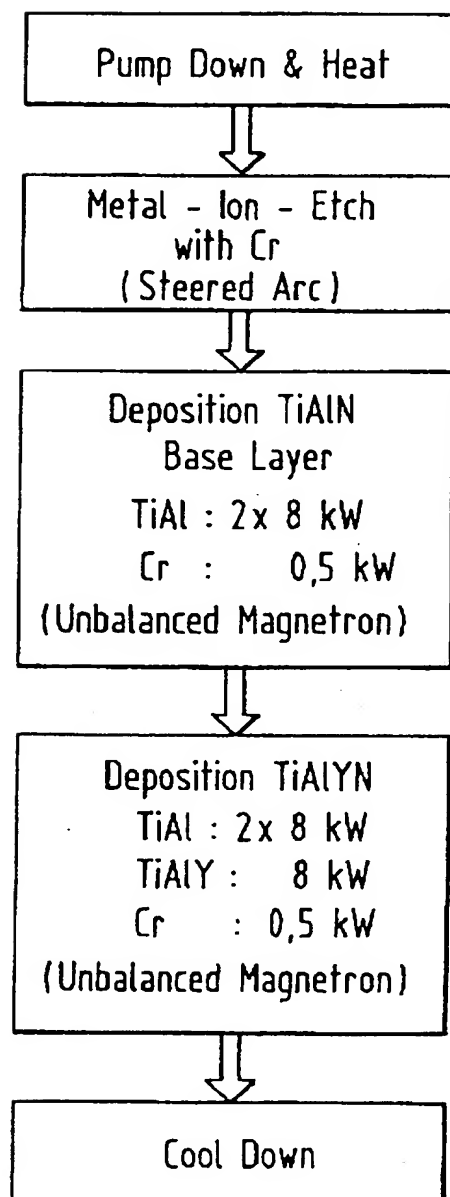
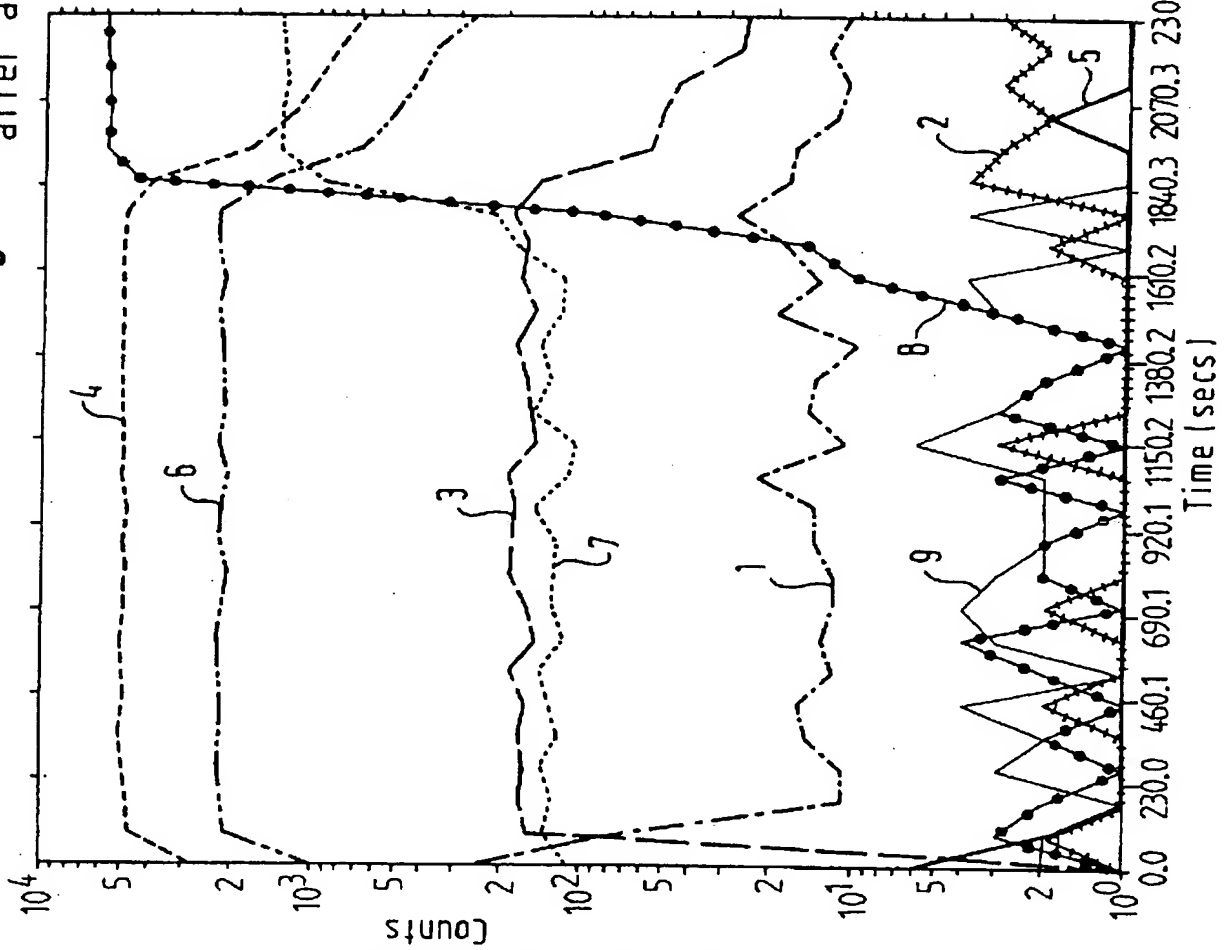


Fig. 3 SNMS profile of a TiAlN coating without Y after a heat treatment in air at 800°C/1 h



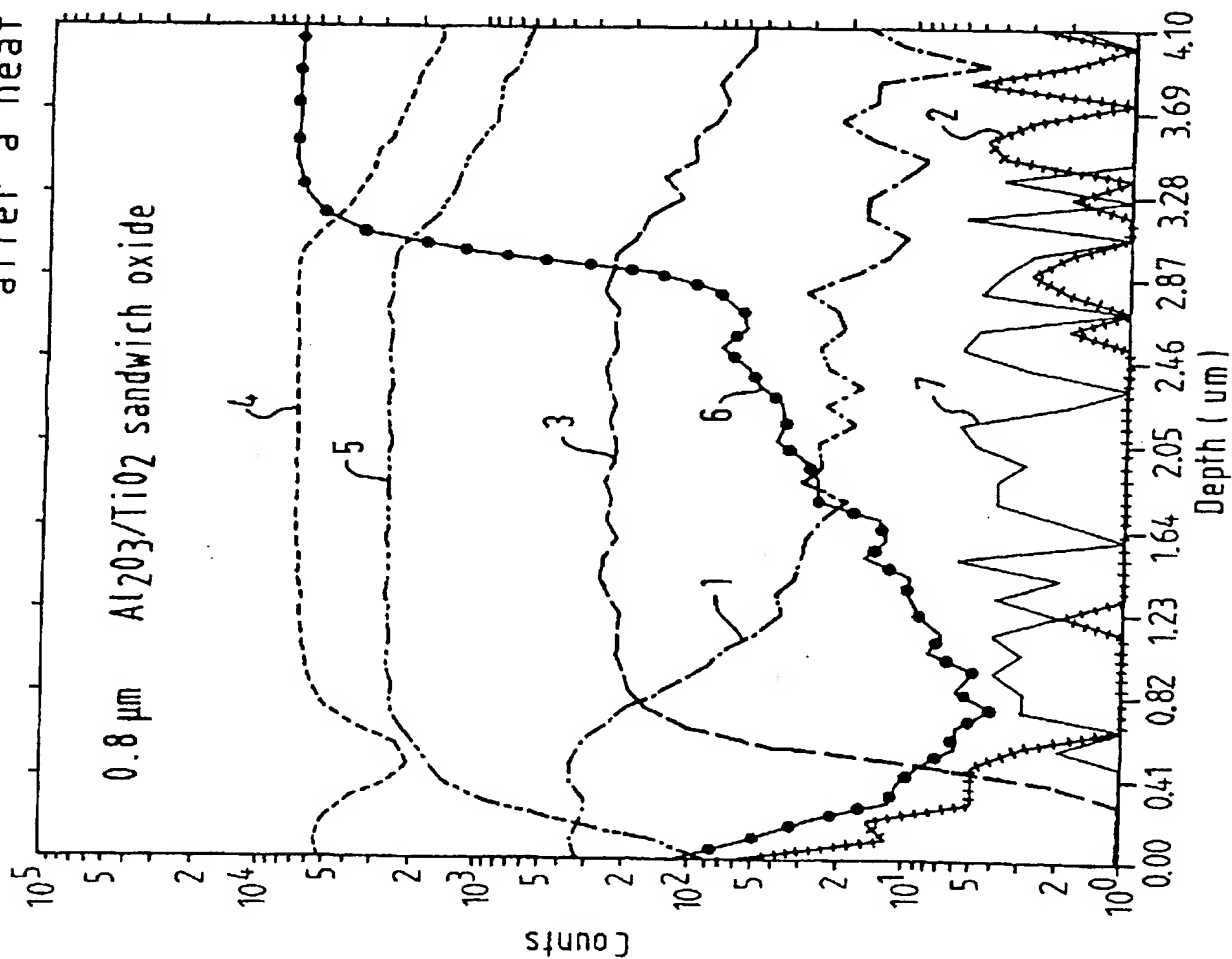
SNMS Depth Profiles

No	Name	Mass	Target Bias (V)	Time (secs)
1	O	16.0	50.0	9.8
2	C	12.0	50.0	9.8
3	N	14.0	50.0	9.8
4	Al	27.0	50.0	9.8
5	Ar	40.0	50.0	9.8
6	Ti	48.0	50.0	9.8
7	Cr	52.0	50.0	9.8
8	Fe	56.0	50.0	9.8
9	Y	89.0	50.0	9.8

Ga+Primary Beam 16keV 150nA  
TiAlN 800C 1hr air SNMS

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Fig. 4 SNMS profile of a TiAlN coating without Y after a heat treatment in air at 900°C/1h

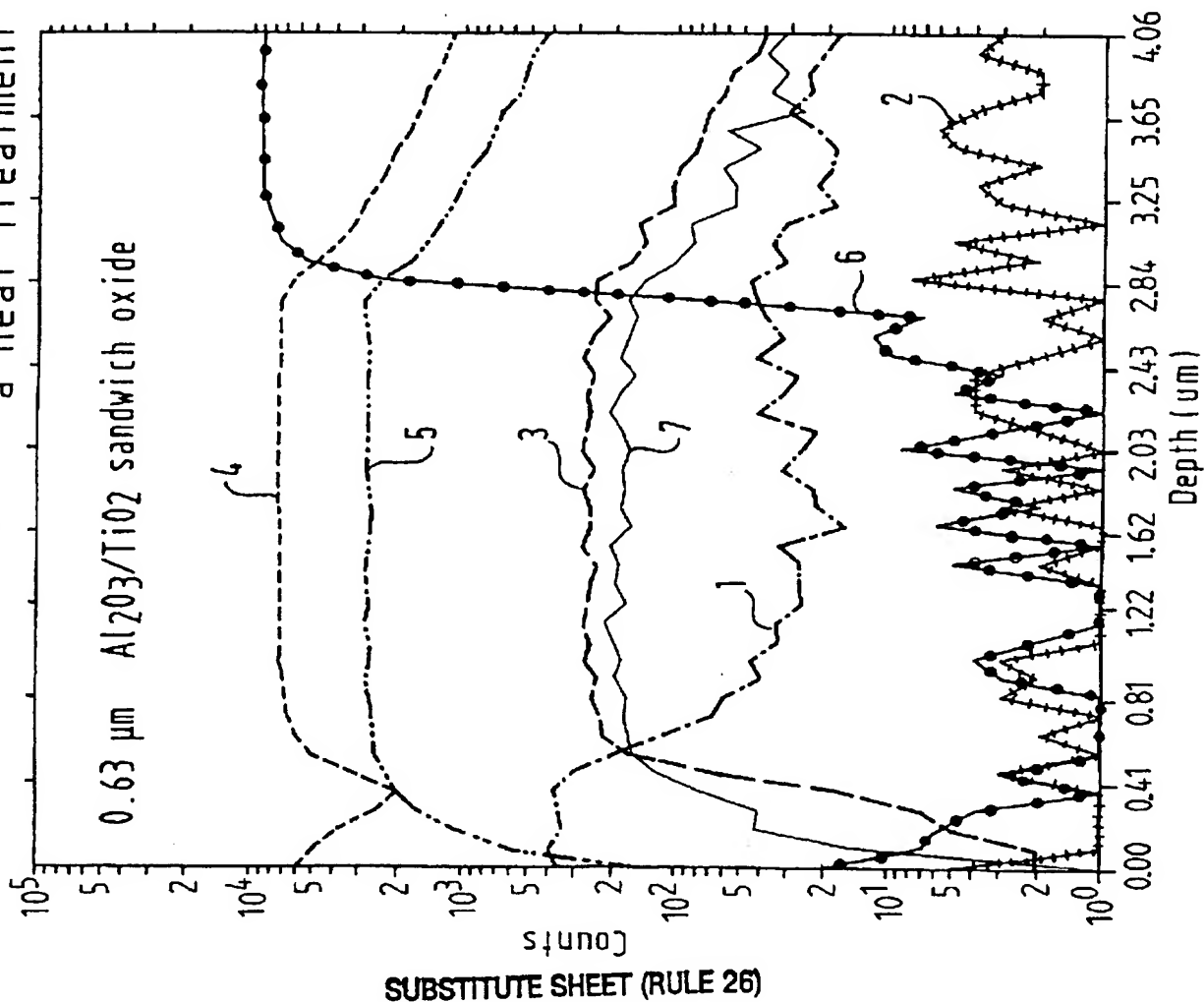


### SNMS Depth Profiles

No	Name	Mass	Target Bias (V)	Time (secs)
1	O	16.0	50.0	9.8
2	C	12.0	50.0	9.8
3	H	14.0	50.0	9.8
4	Al	27.0	50.0	9.8
5	Ti	48.0	50.0	9.8
6	Fe	56.0	50.0	9.8
7	Y	89.0	50.0	9.8
Cr is not displayed				

Ga+ Primary Beam 16keV 150nA  
calibrated from a9000  
#A.9 TiAlN 900C

Fig. 5 SNMS profile of a TiAlYN coating after a heat treatment in air at 900°C/1 h



# SNMS Depth Profiles

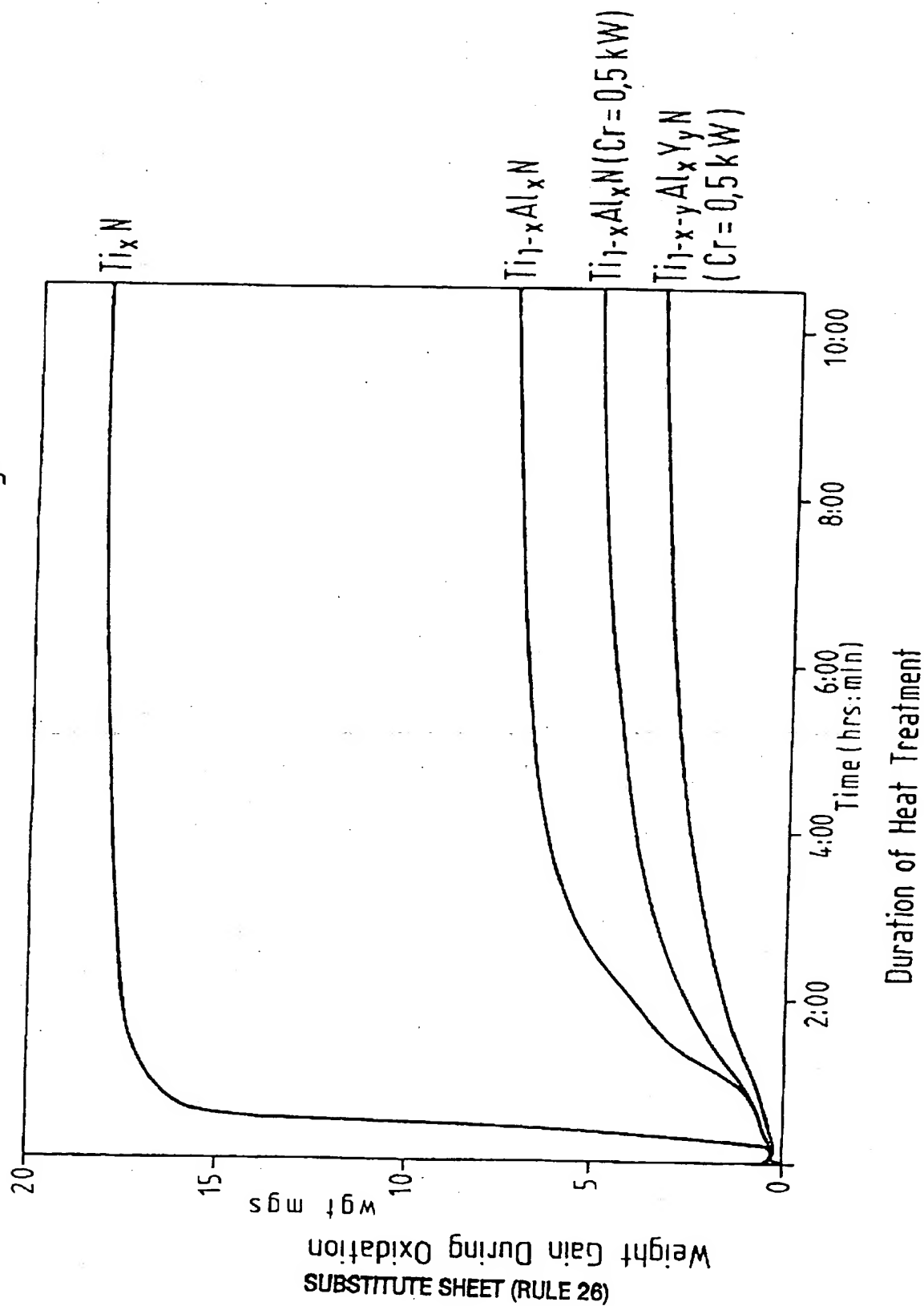
No	Name	Mass	Bias (V)	Target Time (secs)
1	O	16.0	50.0	9.8
2	C	12.0	50.0	9.8
3	N	14.0	50.0	9.8
4	Al	27.0	50.0	9.8
5	Ti	48.0	50.0	9.8
6	Fe	56.0	50.0	9.8
7	Y	89.0	50.0	9.8

Cr is not displayed

Ga+Primary Beam 16keV 150nA  
calibrated from y9000  
#Y.9 TiAlN 900C

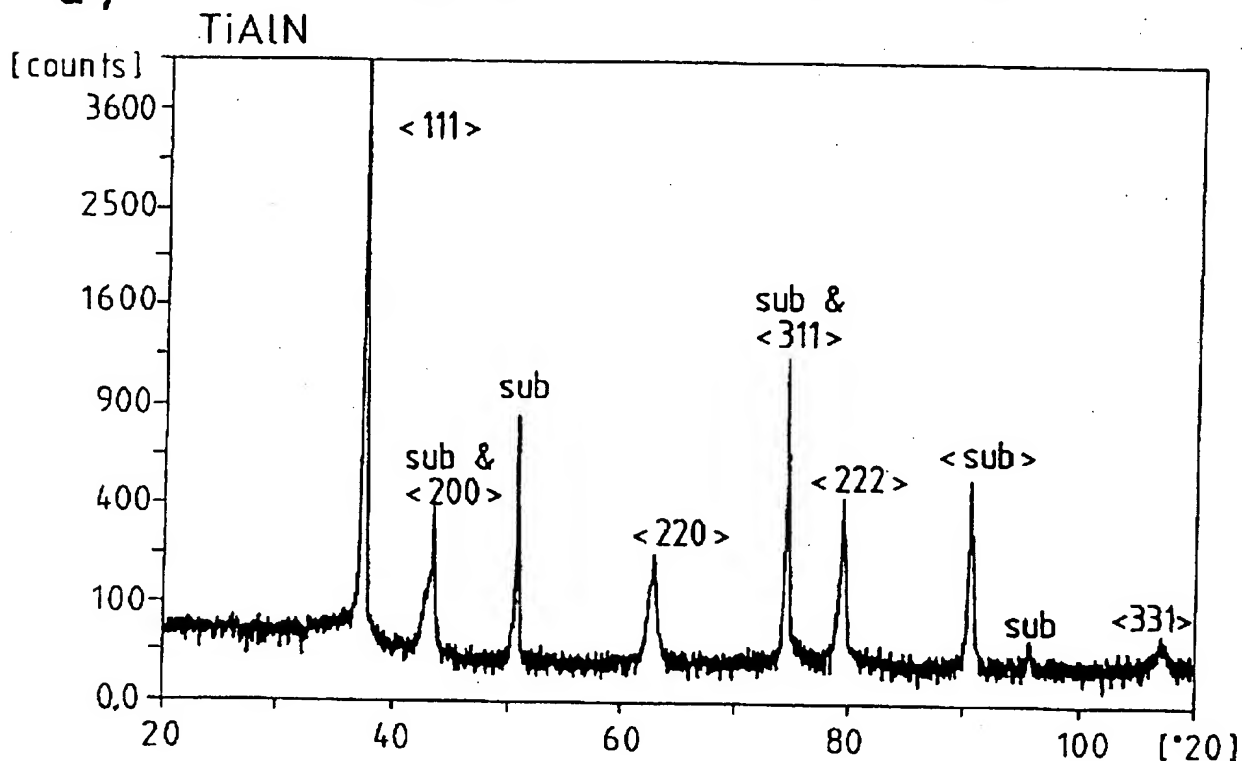


Fig. 6 Isothermat Thermo Gravimetry  
of Various Hard Coatings

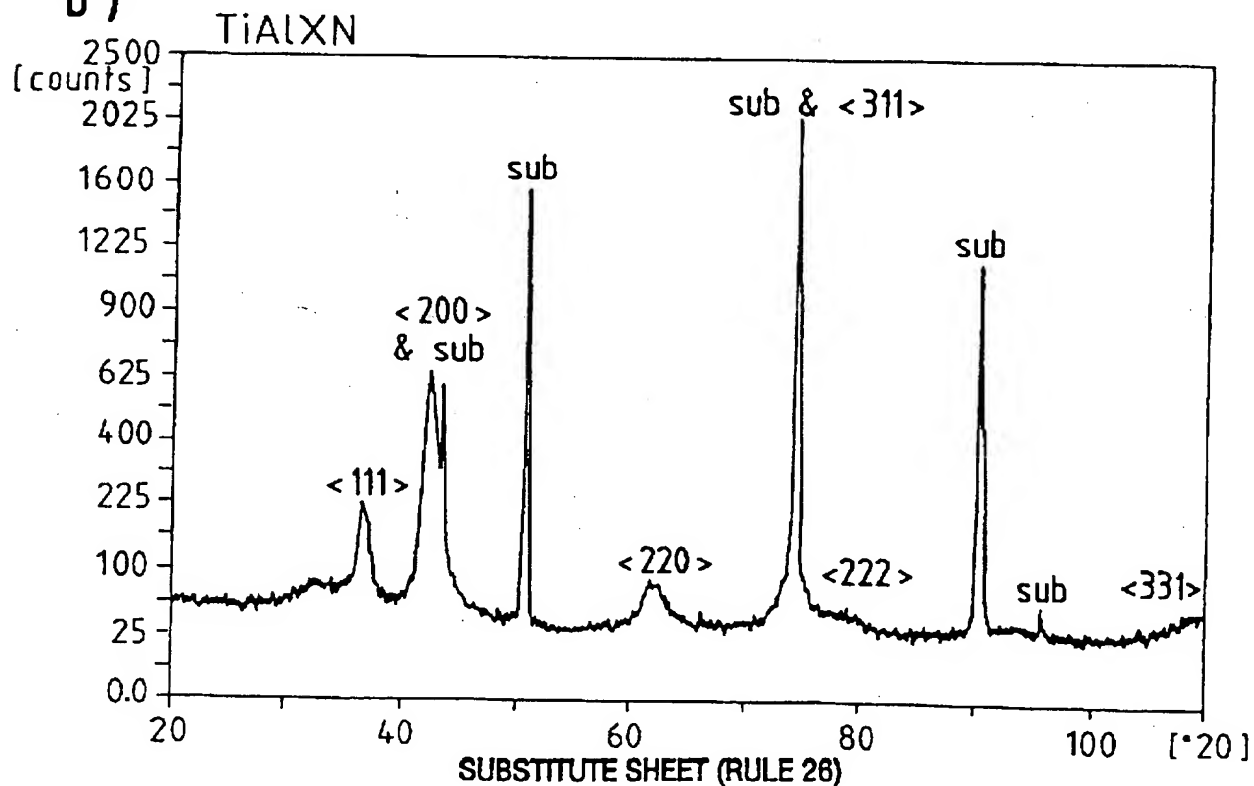


**Fig. 7** XRD Analysis of TiAlN and TiAlYN  
(Polycrystalline B1-NaCl Structure)

a)

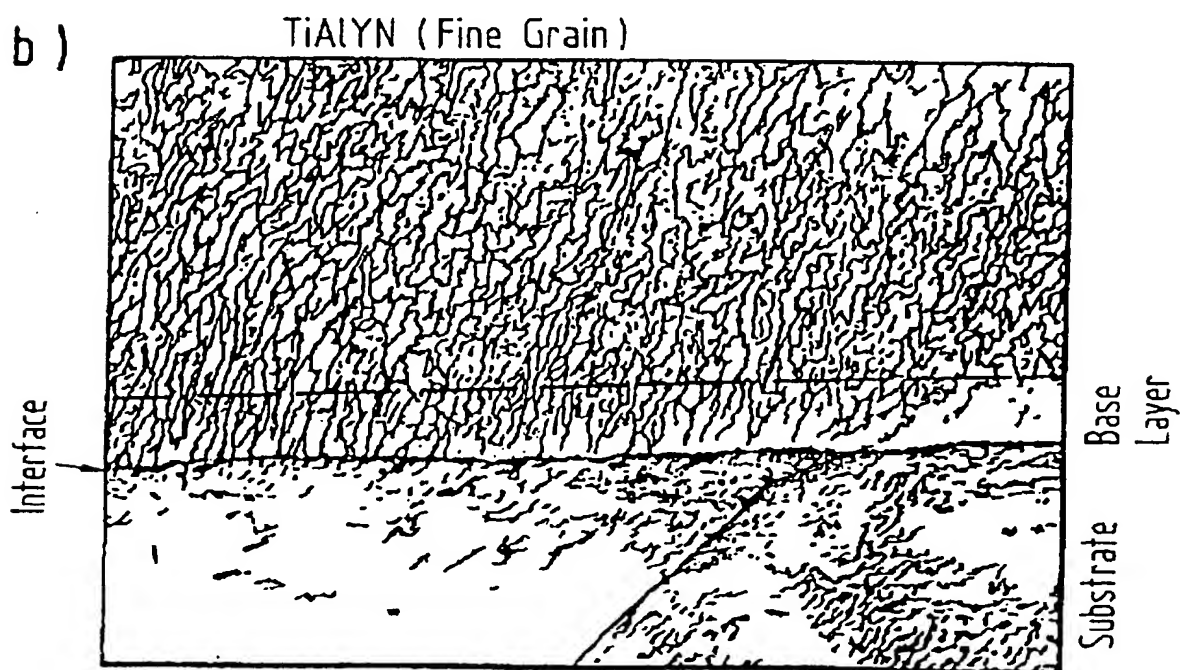
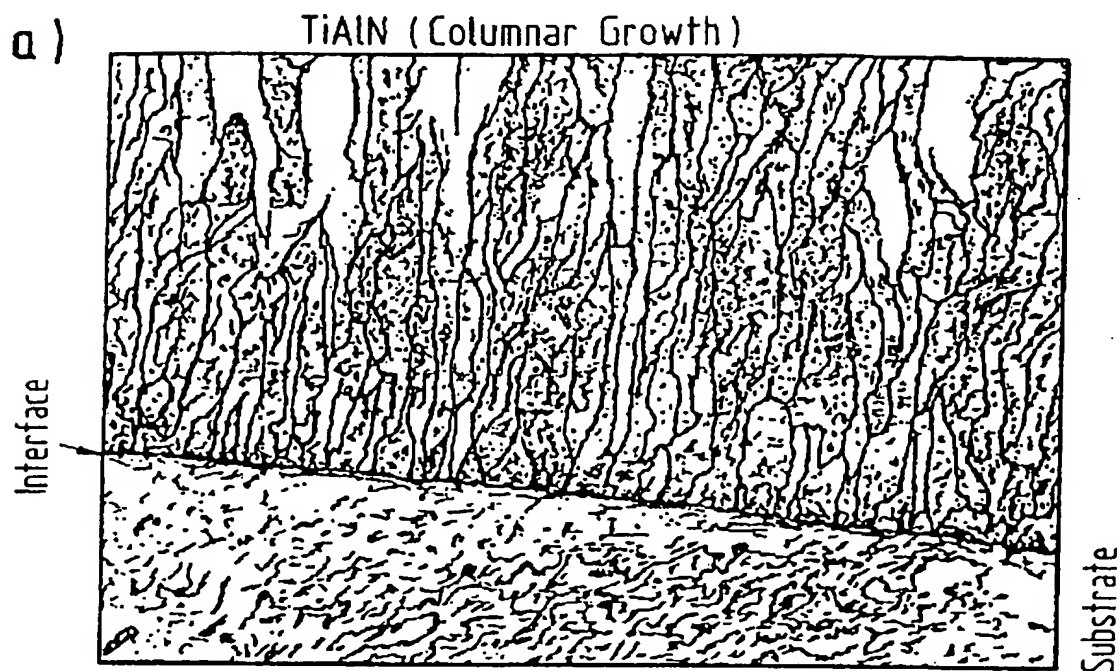


b)



8 / 8

Fig. 8 Computer Processed TEM Cross-Section Images (Magnification: 50000)



SUBSTITUTE SHEET (RULE 26)

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C23C14/06 C23C14/32 C23C14/35

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WERKSTOFFE UND KORROSION, vol. 41, 1990, pages 753-754, XP000673756 W.-D. MÜNZ: "Oxidation resistance of hard wear resistant Ti0,5Al0,5N coatings grown by magnetron sputter deposition" cited in the application see the whole document	1,2
X	JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, vol. 13, no. 5, 1 September 1995, pages 2303-2309, XP000550436 YU Z ET AL: "PREPARATION AND PROPERTIES OF TI(Y)N COATINGS" see the whole document --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 June 1997

Date of mailing of the international search report

24. 06. 97

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/01234

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 007, no. 171 (C-178), 28 July 1983 & JP 58 077564 A (INOUE JAPAX KENKYUSHO KK), 10 May 1983, see abstract ---	1
A	DE 44 05 477 A (HAUZER HOLDING) 24 August 1995 cited in the application see page 2 - page 3; figure 3 ---	18-24
A	JOURNAL OF MATERIALS SCIENCE LETTERS, vol. 10, no. 9, 1 May 1991, pages 503-505, XP000215823 MICHALSKI A: "STRUCTURE AND USEFUL PROPERTIES OF MULTI-COMPONENT TITANIUM NITRIDE OBTAINED BY PULSE PLASMA DEPOSITION" see the whole document ---	13
A	RUSSIAN ENGINEERING RESEARCH, vol. 13, no. 8, 1 January 1993, pages 35-37, XP000458433 SAIDAKHMODOV R KH ET AL: "ION-PLASMA TITANIUM, CHROMIUM, AND VANADIUM NITRIDE-CONTAINING COATINGS" see the whole document ---	13
A	JOURNAL OF APPLIED PHYSICS, vol. 73, no. 12, 15 June 1993, pages 8580-8589, XP000381378 ADIBI F ET AL: "EFFECTS OF HIGH-FLUX LOW-ENERGY (20-100 EV) ION IRRADIATION DURING DEPOSITION ON THE MICROSTRUCTURE AND PREFERRED ORIENTATION OF Ti0.5Al0.5N ALLOYS GROWN BY ULTRA-HIGH-VACUUM REACTIVE MAGNETRON SPUTTERING" see the whole document -----	3-5

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 97/01234

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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